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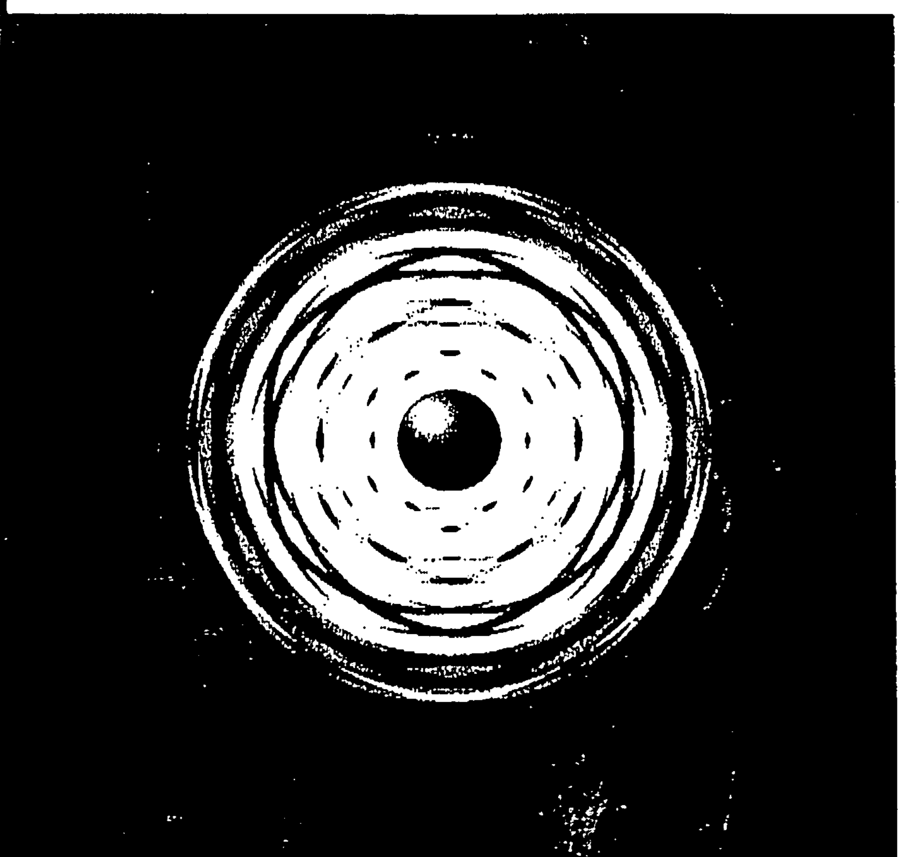

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The Uses of Power Ultrasound in Chemistry and Processing

Power ultrasound has been used for many years in two specific industrial areas: cleaning and plastic welding. Over the last ten years an increasing interest has been shown in its potential for use over a much wider range of chemistry and processing which has been grouped together under the general title of sonochemistry. Most of these uses depend on the generation of acoustic cavitation in liquid media, but this text, while underlining the importance of the physics and mathematics of cavitation, mainly concentrates on applications of the technology.

After an introduction to the topic and some historical background to the uses of power ultrasound, the general principles of acoustic cavitation are explored including some background physics, bubble dynamics and factors which influence cavitation. The remainder of the book incorporates a series of applications of sonochemistry that illustrate the types of physical and chemical effects of ultrasonically induced cavitation which will interest chemists and engineers alike. Amongst the major topics included are chemical synthesis, environmental protection and the remediation of water, sewage and soils, polymer synthesis and processing, electrochemistry including both analytical and synthetic aspects and plating. The final chapter reviews the range of ultrasonic equipment available in the laboratory and the progress made towards the scale-up of sonochemistry.

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Professor Timothy J. Mason
Professor John P. Lorimer
Coventry University
Priory Street
Coventry CV1 5FB
U.K.

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4.2 Water Purification

4.2.1 Biological Decontamination

Water treatment can be broadly divided into two types, wastewater and potable (drinking) water. Sewage treatment plants deal with the treatment of wastewater which consists of sewage, road and agricultural surface run-offs as well as industrial effluent. Potable water treatment produces the final product for human consumption. Primary treatment processes are able to reduce the number of microorganisms in water but they can never ensure complete removal and so final disinfection (polishing) is perhaps the most important stage of water treatment. In Europe and U.S.A. chlorination is widely used but there are problems associated with using this method, these include:

- Microorganisms (especially bacteria) are capable of producing strains which are tolerant to normal chlorine treatment levels. This can be overcome by employing higher chlorine levels; however, this can lead to the formation of unpleasant flavours and odours due to the formation of chlorophenols and other halocarbons.
- Certain species of microorganisms produce colonies and spores which agglomerate in spherical or large clusters. Chlorination of such clusters may destroy microorganisms on the surface leaving the innermost organisms intact.
- Fine particles such as clays are normally removed by flocculation using chemicals such as aluminium sulphate. The flocs can entrap bacteria and their spores protecting them from chlorination. The vast majority of floc particles are removed during processing but if one or two pass through the system the entrapped bacteria will be unaffected by the final disinfection stage.

4.2.1.1 The Mechanisms of Ultrasonic Action on Cellular Material

In the 1960's research was targeted at understanding the mechanism of ultrasound interaction with microbial cells [1]. Cavitation phenomena and associated shear disruption, localised heating and free radical formation were found to be primary causes. By 1975, it was shown that brief exposure to ultrasound caused a thinning of cell walls attributed to the freeing of the cytoplasm membrane from the cell wall [2]. The types of apparatus used for this purpose were acoustic horn (probe) systems operating at 20 kHz. These were the forerunners of the modern acoustic horns routinely used for the sonication of cell suspensions in order to release their contents without at the same time destroying or denaturing them. Several theories have been proposed

to describe the mechanism of cell damage through exposure to ultrasound, some physical or mechanical and others more chemical in nature. All of them have their origin in cavitation.

The mechanical effects of power ultrasound on chemical systems in a liquid medium are mainly attributed to cavitation and these same forces have a dramatic effect on biological systems [3]. The imploding bubble produces high shear forces and liquid jets in the solvent that may also have sufficient energy to physically damage the cell wall/membrane. Mechanical effects of this type have been used on a small scale for the disinfection of water contaminated with microbial spores *e.g. cryptosporidium* although the acoustic energy required is high [4]. Such collapse will also produce free radical species which are also capable of killing microorganisms.

On the other hand stable cavitation (bubbles that oscillate in a regular fashion for many acoustic cycles) induce microstreaming in the surrounding liquid which can also induce stress in any microbiological species present [5]. This type of cavitation may well be important in a range of applications of ultrasound to biotechnology [6]. An important consequence of the fluid micro-convection induced by bubble collapse is a sharp increase in the mass transfer at liquid-solid interfaces. In microbiology there are two zones where this ultrasonic enhancement of mass transfer will be important. The first is at the membrane and/or cellular wall and the second is in the cytosol i.e. the liquid present inside the cell.

Most ultrasonic experiments are carried out in temperature controlled systems to ensure that isothermal conditions are maintained. Even a small general increase in microbial temperature can influence both the active and passive transport systems of the cell membrane/wall and this in turn may lead to an increased uptake of compounds. If the temperature is not controlled then sonication could result in a large temperature increase which will lead to the denaturation (deactivation) of enzymes, proteins and other cellular components present within the microorganism [7].

The effects of ultrasound upon the permeability of the cell walls of the gram-negative bacteria *Pseudomonas aeruginosa* toward hydrophobic compounds particularly antibiotics have been examined [8]. The penetration and distribution of 16-dosylstearic acid (16-DS) in the cell membranes of the bacteria was quantified by a spin-labeling electron spin resonance (ESR) method. The results indicated that the intracellular concentration of 16-DS was higher in insonated cells and increased linearly with the sonication power. ESR spectra indicated that ultrasound enhanced the penetration of 16-DS into the structurally stronger sites of the inner and outer cell membranes. The effect of ultrasound on the cell membranes was transient in that the initial membrane permeability was restored upon termination of the ultrasound treatment. These results suggested that the resistance of gram-negative bacteria to the action of hydrophobic antibiotics was caused by a low permeability of the outer cell membranes and that this resistance may be reduced by the simultaneous application of antibiotic and ultrasound.

At an appropriate intensity level of ultrasound, intracellular microstreaming has been observed inside animal and plant cells with rotation of organelles and eddying motions in vacuoles of plant cells [9]. These effects can produce an increase in the metabolic functions of the cell that could be of use in both biotechnology and microbiology, especially in the areas of biodegradation and fermentation.

Cavitation induced in any liquid system will result in the formation of radicals (see Section 4.2.2). In the case of water sonication one chemical product is hydrogen peroxide which, together with the radical species provides a powerful bactericide and oxidant.

4.2.1.2 Ultrasonic Destruction of Biological Contaminants in Water

In order to achieve complete destruction of biological contaminants in water through sonication very high ultrasonic intensities are necessary. Unfortunately this makes the technique expensive to use for general microbiological decontamination. However over the last two decades some conventional disinfection techniques involving chemicals, ultraviolet light and heat treatment have become less effective as some bacteria become more resistant. Such processes have become a focus for the use of sonication as an adjunct to other techniques.

Low power ultrasound offers the possibility of enhancing the effects of chlorine. The results of a study of the combined effect of low power ultrasound and chlorination on the bacterial population of raw stream water are shown (Tab. 4.2). Neither chlorination alone nor sonication alone was able to completely destroy the bacteria present. When sonication is combined with chlorination however the biocidal action is significantly improved [10]. The effect can be ascribed partly to the break-up and dispersion of bacterial clumps and flocs which render the individual bacteria more susceptible to chemical attack. In addition cavitation induced damage to bacterial cell walls will allow easier penetration of the biocide.

A continuing problem in water treatment is the occurrence of algal blooms. Algae may be killed relatively easily on exposure to ultrasound and a lightly "polluted" system

Tab. 4.2. The effect of ultrasound and chlorination on bacterial growth.

Treatment	% Bacteria kill	
	after 5 min	after 20 min
No treatment	0	0
Chlorine, 1 ppm	43	86
Ultrasound alone	19	49
Ultrasound in the presence of 1 ppm chlorine	86	100

Conditions: 1:10 dilution of raw stream water, using ultrasonic bath (power input to system 0.6 W cm^{-3}), T = 20 °C.

provides very little attenuation to sound transmission. In such cases it is possible to use high frequency ultrasound which can be operated at low power. High frequency ultrasound has been shown to give high radical activity at the interface between liquids and gases (as shown through sonoluminescence measurement). Logically then if a large number of small bubbles were introduced into a field of high frequency ultrasound there would be a very large gas/liquid surface area for cavitational activity and the bubbles themselves should also provide "seeds" for cavitation events. This is the basis of an approach to algae removal and control proposed by the Belgian company Undatim [11]. In a trial involving the monocellular algae species Scenedesmus Capricornutum some spectacular results were obtained. A cell was constructed to treat water at a rate of $2\ m^3\ h^{-1}$ using an acoustic power of 450 W. At a temperature of 25 °C a single pass through the cell of a deep green, highly concentrated, solution of the algae containing some 4×10^6 algal cells per cm^3 reduced the recovery threshold of the microorganism by some 60 %. This indicates that the treatment even operating at algal concentrations that are far higher than might be encountered in normal treatments offers the potential not only to kill the microorganism but also to severely restrict its reproductive ability.

This ultrasonic anti-algae methodology has been combined with an electromagnetic anti-scaling treatment to provide a new global water remediation technology for half-closed circuits, e. g. cooling towers, known as Sonoxide [12]. This process tackles two major problems of cooling circuits, namely the build up of scale and algae. These are solved with a minimal energy requirement, without the need to use soft water and without the addition of chemicals.

Many microorganisms have the ability to form resistant and dormant structures when subjected to a stress which are known as either spores or cysts. Spore production is a phenomenon amongst some species of microorganisms. Spores have two functions (a) as an agent for dispersal of the organism and (b) as a method for its survival during adverse conditions. Fungal spores are abundant in the foam of rivers and streams through which they are dispersed. To ensure spore survival they must be more resistant to adverse conditions than their parent cell to ensure dormancy occurs after its formation. Some spores have a very long life e. g. *anthrax* spores in the soil can live for over 50 years. The bacterial endospore literally represents suspended animation, and can germinate when conditions for growth are ideal. The endospores of *Bacillus* and *Clostridium* species are of extreme importance to man; for example *Bacillus thermophilus* spores are only destroyed by heating at 100 °C for 4 h. Spores possess a great resistance to desiccation (removal of water from cell), ultraviolet light, chemical and enzymatic attack. It is obvious therefore that any water treatment techniques should not only be able to destroy microorganisms but also be able to destroy or remove any of the much more difficult to kill spores which might be present.

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The potozoa, *Cryptosporidium parvum*, is the cause of a water-borne disease called cryptosporidiosis which causes severe upset of the digestive system in humans and which can be particularly serious in young children and the elderly. Many cases have been reported in the last decade. Outbreaks have occurred throughout Europe as well as the USA and are not only associated with the developing countries. The main concern of water suppliers is that conventional treatment methods are inadequate and are not a sufficient barrier in preventing the water-borne transmission of cryptosporidiosis. *Cryptosporidium parvum* forms spores known as oocysts which have a very thick outer wall. This prevents or makes it very difficult for normal disinfectants to penetrate into the oocyst. The most commonly used disinfectant techniques in water treatment i.e. chlorination and ultraviolet light are ineffective but ozone seems to be able to destroy some of these oocysts. The use of ultrasound as an aid for the disinfection of water contaminated with *cryptosporidium* oocysts has been evaluated at Coventry University [13]. It was found that sonication reduced the number of oocysts by 25 % in 2 min. And more importantly the proportion of oocysts rendered non-viable increases with duration of sonication. Similar work has been carried out by Leeds University in conjunction with Biwater and their findings have been released as part of a patent [4]. It is however clear that the power required for the complete removal of oocysts in mains water treatment will be extremely high.

Although the predominant efforts in biological decontamination has been aimed at water treatment, sonication has also been investigated in food sterilisation. Heat treatment is one of the most frequently used methods for stabilising foods because of its ability to inactivate enzymes and destroy microorganisms. However, since heat can also alter many organoleptic properties and diminish the content or availability of some nutrients, there is a growing interest in searching for methods that are able to stabilise foods with little or no heat added. The first report on the synergy between ultrasound and heat as a mechanism for killing the vegetative bacterium *Staphylococcus aureus* was published by a Spanish group [14]. They found that the use of power ultrasound allowed a reduction in the effective temperatures at which sterilisation could be achieved. Thermosonication is the term now given to the combined application of heat and ultrasound and it was found to reduce the concentration of *Bacillus subtilis* spores by up to 99.9 % in the 70 to 90 °C range in a small scale ultrasonic reactor using a 20 kHz, 150 W ultrasound source [15]. Work carried out at Coventry University has addressed the issues of the effect of the food substrate (orange juice, milk and rice pudding) on the thermosonication phenomenon using a range of organisms (*Zygoillus polymyxa*) [16]. The studies confirmed the synergistic effect of ultrasound and heat thus in milk, the heat resistance (*D* value) of *L monocytogenes* was approx. 6-fold lower at 60 °C when sonicated at 20 kHz and the *D* value of *Z. bailii* in orange juice was approx. 10-fold lower at 55 °C when sonicated at 38 kHz.